

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

High Coercivity in Co/Pt Multilayers

J.-H. KIM and S.-C. SHIN, *Jpn. J. Appl. Phys.*, 1996, 35, (1B), 342-345

The coercivity in a Co/Pt multilayer on a Si₃N₄ underlayer increased more than two-fold when using a rotating substrate. The increase was due to the enhancement of domain wall pinning effects caused by an increase of surface roughness in the Si₃N₄ underlayer. The Si₃N₄ underlayer surface prepared on a rotating substrate was rougher than that on a stationary substrate, which may be due to the oblique incidence of sputtered materials onto the rotating substrate.

Long-Range Order and Magnetic Properties of Mn_xPt_{1-x} Thin Films

K. W. WIERMAN and R. D. KIRBY, *J. Magn. Magn. Mater.*, 1996, 154, (1), 12-16

Thin films of Mn_xPt_{1-x} ($x = 0.18, 0.22, 0.25, 0.30, 0.34$) prepared by magnetron sputtering onto quartz substrates were annealed in vacuum for 1 h at 850°C. After annealing, XRD showed the films to have the Cu₃Au cubic structure and be highly textured with the (111) axis along the film normal. The films displayed a high degree of long-range order, shown by the ratio of the intensities of the superlattice (100) and fundamental (200) XRD reflections.

Growth of Ultrathin Pd Films on Al(001) Surfaces

V. SHUTTHANANDAN, A. A. SALEH, N. R. SHIVAPARAN and R. J. SMITH, *Surf. Sci.*, 1996, 350, (1-3), 11-20

The growth mode and the interface structure of ultrathin Pd films deposited on Al(001) surfaces were determined at room temperature. Pd atoms intermixed with and displaced Al substrate atoms. The mixing continued for Pd coverages from 0-5 monolayers, when a Pd metal film began to grow on the alloy surface. XPS indicated that AlPd formed during mixing, followed by the formation of Pd metal.

Effects of Y₂BaCuO₇ and Platinum Additions on the Unidirectional Solidification of YBa₂Cu₃O_{7-δ}

L. DURAND, D. DIERICKX, P. RÉGNIER, O. VAN DER BIEST and S. POISSONNET, *Supercond. Sci. Technol.*, 1996, 9, (4), 290-296

The effects of 211 and/or Pt additions on the solidification of YBaCuO was studied. Mixing the pure 123 powder with 20 wt.% very fine (1 μm) and regular sized Pt 211 particles strongly increased the viscosity of the peritectic liquid and resulted in a dramatic refinement in the distribution of the 211 particles trapped in the 123 matrix of the samples. Extra addition of 0.5 wt.% Pt further refined this distribution.

Magnetic Excitations and the Search for Crystal-Field Transitions in the Heavy-Fermion Superconductor UPd₂Al₃

A. KRIMMEL, A. LOIDL, R. ECCLESTON, C. GEIBEL and F. STEGLICH, *J. Phys.: Condens. Matter*, 1996, 8, (11), 1677-1685

Crystalline-electric field (CEF) excitations in the antiferromagnetic heavy-fermion superconductor UPd₂Al₃ were studied by inelastic neutron scattering. UPd₂Al₃ is an example of 5f-electron systems with a residual line width which corresponds to the macroscopically estimated Kondo lattice temperature. However, significant deviations from this suggest additional inelastic contributions that persist up to $T = 150$ K. This additional scattering could be due to CEF excitations or intersite magnetic correlations.

Superconductivity in Heavy-Fermion CeRh₂Si₂

R. MOVSHOVICH, T. GRAF, D. MANDRUS, J. D. THOMPSON, J. L. SMITH and Z. FISK, *Phys. Rev. B*, 1996, 53, (13), 8241-8244

A superconducting transition in the heavy-fermion compound CeRh₂Si₂ was discovered under hydrostatic pressure of $> \sim 9$ kbar, near the critical pressure needed to suppress antiferromagnetic order ($T_N(P=0) = 36$ K). Superconductivity occurred at ~ 350 mK. Magnetic AC susceptibility showed a diamagnetic response corresponding to $\sim 1\%$ of perfect diamagnetism.

The Effect of Si/Ir Codeposition Ratio on the Ir Silicide/Si(100) Interface Roughness

C. K. CHUNG and J. HWANG, *Mater. Chem. Phys.*, 1996, 43, (2), 191-194

The effect of the Si/Ir codeposition ratio on Ir silicide/Si(100) interface roughness was studied on Ir silicides grown on Si(100) by codeposition at Si/Ir atomic ratios of 0, 1 and 2 at 450°C under UHV. Epitaxial Ir₃Si₄ grew on Si(100) as pure Ir was deposited at all deposition ratios. The Ir₃Si₄/Si(100) interface remained smooth, although intermixing occurred during deposition, but at higher deposition ratios the Ir₃Si₄/Si(100) interface became rougher.

Electrical Conductivity and Superconductivity of Metal Phosphides with Skutterudite-Type Structure Prepared at High Pressure

I. SHIROTANI, T. ADACHI, K. TACHI, S. TODO, K. NOZAWA, T. YAGI and M. KINOSHITA, *J. Phys. Chem. Solids*, 1996, 57, (2), 211-216

NiP₃, LaRu_{4-x}Os_xP₁₂ ($x = 0, 1, 2, 3, 4$) and CeRu₄P₁₂ phosphides with skutterudite (CoAs₃)-type structure were prepared at around 1100°C and 4 GPa using a wedge-type cubic-anvil high pressure apparatus. Superconductivity was observed in LaRu₄P₁₂, LaRu₃OsP₁₂ and LaRu₂Os₂P₁₂ at ~ 7 K. The upper critical field of LaRu₄P₁₂ was 3.65 T at 0 K.

Quantum Oscillations in the Layered Perovskite Superconductor Sr_2RuO_4

A. P. MACKENZIE, S. R. JULIAN, A. J. DIVER, G. J. MCMULLAN, M. P. RAY, G. G. LONZARICH, Y. MAENO, S. NISHIZAKI and T. FUJITA, *Phys. Rev. Lett.*, 1996, 76, (20), 3786–3789
A comprehensive study is presented of observed magneto-oscillatory phenomena in the normal state of Sr_2RuO_4 , which is the first layered perovskite superconductor ($T_c \cong 1$ K) not based on Cu. All sheets of the Fermi surface, including the large ones, have been observed, thus permitting consistent correlation of a number of physical properties. The observations are compatible with a Fermi liquid, which may be linked with coherent interplane transport at low temperatures.

CHEMICAL COMPOUNDS

Size-Evolution Towards Metallic Behavior in Nano-Sized Gold and Platinum Clusters as Revealed by ^{197}Au Mössbauer Spectroscopy

F. M. MULDER, R. C. THIEL, L. J. DE JONGH and P. C. M. GUBBENS, *NanoStructured Mater.*, 1996, 7, (3), 269–292

^{197}Au Mössbauer spectroscopic studies were made on the large Pt_{300} cluster and four types of molecular Au_n clusters, with different types of ligands, using ^{197}Au produced by neutron activation. The ligands had a large effect on the charge densities at the surface atoms of the cluster cores. For the Pt_{300} compound, the inner core atoms had the same charge density at the nucleus as in the bulk metal. The inner core of the Pt_{300} cluster is metallic, but the Au_n cluster is not.

On a New Oxoiridate(V) of the Sr_4PtO_6 -Type: $\text{NaSr}_4\text{IrO}_6$

S. FRENZEN and H. MÜLLER-BUSCHBAUM, *Z. Naturforsch. B*, 1996, 51, (2), 225–228

X-ray studies were performed of single crystals of $\text{NaSr}_4\text{IrO}_6$ prepared by heating mixtures of Na_2O_2 , SrO and Ir in closed Ag tubes. $\text{NaSr}_4\text{IrO}_6$ crystallises with trigonal (rhombohedral) symmetry in the space group $D_{3d}^6 - R\bar{3}c$ with $a = 9.636(2)$, $c = 11.556(3)$ Å, $Z = 6$, and is isotypic to compounds of the Sr_4PtO_6 type. The substitution of Sr^{2+} by Na^+ in $\text{NaSr}_4\text{IrO}_6$ resulted in an ordered metal distribution and in an increase of the oxidation state from Ir^{IV} to Ir^{V} .

Synthesis and Spectral Studies of 1,3-Diketone Derivatives of *ortho*-Palladated α -Arylalkylamines

V. V. DUNINA, O. A. ZALEVSKAYA, S. P. PALII, D. V. ZAGOREVSKII and YU. S. NEKRASOV, *Izv. Akad. Nauk, Ser. Khim.*, 1996, (3), 733–740

Acetylacetonato derivatives of a series of *ortho*-palladated secondary and tertiary α -arylalkylamines were prepared and characterised. An unusual rearrangement involving migration of an H atom from the alkyl aminoalkyl group to the Pd atom leading to a hydride intermediate and followed by PdH elimination was observed. This may be due to isomerisation of $\eta^2\text{-O, O'}$ -co-ordinated β -diketonate ligand into the $\eta^1\text{-C}$ -bonded diketonyl form, to give the unsaturated metal centre.

Spectroscopic and Electrochemical Investigation of Mixed-Valence $\text{Rh}^{\text{I}}\text{-Rh}^{\text{III}}$ Complexes with Cyanide Bridge

T. V. MAGDESIEVA, S. I. GOREL'SKY, K. P. BUTIN, A. A. BEZRUKOVA, V. S. KHANDKAROVA and YA. S. VYGODSKII, *Izv. Akad. Nauk, Ser. Khim.*, 1996, (3), 726–731

New mixed valence $\text{Rh}^{\text{I}}\text{-Rh}^{\text{III}}$ complexes with cyanide bridges were studied using electronic spectra and redox potentials. Interaction between Rh atoms in the complexes is small (the “fixed valences” case). Intervallence transition from Rh^{I} to Rh^{III} were not observed in the 7000–50,000/cm region. Some of the complexes in the solid state have additional absorption bands in diffuse reflectance spectra due to the interaction of the $\text{Rh}(\text{I})$ group orbitals of appropriate symmetry.

Synthesis and Characterization of Superstructured Rhodium Porphyrins

H. R. JIMÉNEZ and M. MOMENTEAU, *Inorg. Chim. Acta*, 1996, 244, (2), 171–177

Three Rh “two-face” hindered porphyrins were synthesised by the metallation of “basket-handle” porphyrins in dimethylformamide, for example, $[\text{e-BHP}(\text{C}_{12})_2\text{Rh}^{\text{III}}(\text{L})(\text{H}_2\text{O})]\text{Cl}$, etc., where $\text{e-BHP}(\text{C}_{12})_2 = \alpha 5,15:\beta 10,20\text{-bis}[2,2'\text{-}(\text{dodecamethyleneoxy})\text{-diphenyl}]\text{porphyrinato dianion}$ and $\text{L} = \text{dimethylamine}$. In these new neutral or cationic Rh porphyrins, the two faces of the porphyrin are protected by two chains linked at the opposite phenyl rings. Studies of the derivatives of these porphyrins show different reducing tendencies, which follow in general the order for the axial ligand $\text{NH}(\text{CH}_3)_2 > \text{H}_2\text{O}$ or Cl^- .

The Activation of C-H Bonds via Ru-Ru Bond Fission

A. J. BLAKE, P. J. DYSON, P. E. GAEDE and B. F. G. JOHNSON, *Inorg. Chim. Acta*, 1996, 241, (2), 11–12

New metallacyclic cluster, $\text{Ru}_3(\text{CO})_8(\text{C}_6\text{H}_6)$ (1) is produced in low yield by heating the $\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)$ cluster in heptane under reflux. In (1), the fission of a Ru-Ru bond induced the cleavage of two C-H bonds with the concomitant formation of two Ru-C σ bonds. ^1H NMR spectra show the two H atoms lost in the reaction are the most activated of those present on the ligand, giving resonances at 0.88 and 1.56 ppm, which are low compared with ~ 7 ppm for the free ligand.

A Chain Complex of Ruthenium(II,III) Cation Dimer Linked by a Nitroxide Radical, $[\text{Ru}_2(\text{O}_2\text{CCMe}_3)_4(\text{NITPh})]_n(\text{BF}_4)_n$ (NITPh = 2-Phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide)

M. HANDA, Y. SAYAMA, M. MIKURIYA, R. NUKADA, I. HIROMITSU and K. KASUGA, *Chem. Lett. Jpn.*, 1996, (3), 201–202

The above Ru chain complex was characterised by the X-ray analysis, showing a structure with the alternated alignment of $S = 3/2$ ($\text{Ru}(\text{II,III})$ core) and $S = 1/2$ (NITPh). The magnetic moment decreased monotonically with decreasing temperature. This chain complex has a paramagnetic dimetal centre with a metal-metal bond linked by the nitroxide radical.

ELECTROCHEMISTRY

Electro-oxidation of Cl Molecules at Pt-Based Catalysts Highly Dispersed into a Polymer Matrix: Effect of the Method of Preparation

W. T. NAPPORN, H. LABORDE, J.-M. LÉGER and C. LAMY, *J. Electroanal. Chem.*, 1996, 404, (1), 153–159

Highly dispersed Pt-based electrodes modified with Ru and/or Sn inserted in a conducting polymer matrix exhibited weak poisoning effects compared with pure Pt particles. The Pt-Ru alloy was the most promising catalyst for the electro-oxidation of MeOH, while Pt-Sn electrodes gave a very significant negative shift to the oxidation potentials during electro-oxidation of formaldehyde and formic acid. An important decrease in poisoning was found mainly with Pt-Sn electrodes, but also with Pt-Ru and Pt-Ru-Sn electrodes.

The Electrooxidation of Formaldehyde on Pt(100) and Pt(110) Electrodes in Perchloric Acid Solutions

P. OLIVI, L. O. S. BULHÕES, J.-M. LÉGER, F. HAHN, B. BEDEN and C. LAMY, *Electrochim. Acta*, 1996, 41, (6), 927–932

Studies of the electro-oxidation of formaldehyde on Pt(100) and (110) electrodes in a perchloric acid medium showed both undergo two oxidation processes involving either methylene-glycol oxidation or adsorbed CO formation. The Pt(100) electrode is more active for the methylene-glycol oxidation. The CO species were adsorbed linearly on both electrode surfaces, but multibonded and bridge bonded CO forms were only present on the Pt(100). The adsorbed CO species block the surfaces during methylene-glycol oxidation, with Pt(110) being more blocked than Pt(100).

Hydrogen Evolution Reaction in Alkaline Solution. Catalytic Influence of Pt Supported on Graphite vs. Pt Inclusions in Graphite

J. FOURNIER, L. BROSSARD, J.-Y. TILQUIN, R. CÔTÉ, J.-P. DODELET, D. GUAY and H. MÉNARD, *J. Electrochem. Soc.*, 1996, 143, (3), 919–926

Electrochemical behaviour of Pt having graphite powders bonded by polymerised LaPO₄ was studied for the HER in 1 M KOH solution. Pt-supported electrodes, Pt(s)/C/LaPO₄ (1) were more active than those containing Pt inclusions in graphite, Pt(i)/C/LaPO₄ (2). In high-current-density conditions of 0.25 A/cm², (2) was stable while (1) disintegrated after 24 h.

Fabrication of Pt/(Ta₂O₅+Pt) Coated Titanium Electrodes Using Combination of Partial Thermal Decomposition and Electrolytic Reduction of Pt and Ta complex

Y. KAMEGAYA, J. SAITO, H. KOBAYASHI, M. OKUYAMA and T. MITAMURA, *Denki Kagaku*, 1996, 64, (2), 138–142

A three-layered Pt/(Ta₂O₅+Pt)/Ti electrode was fabricated, to protect the Ti substrate from corrosion, by partial thermal decomposition (1) and electrolytic reduction of Pt(NO₂)₂(NH₃)₂, and (1) of Ta(OC₂H₅)₅. The interlayer is amorphous Ta₂O₅, and Pt, with a Pt top layer. It has excellent stability during anodic O₂ evolution in H₂SO₄, high conductivity and durability.

A New Successive System for Hydrogenation of Styrene Using a Two-Compartment Cell Separated by a Pd Sheet Electrode

C. IWAKURA, T. ABE and H. INOUE, *J. Electrochem. Soc.*, 1996, 143, (4), L71–L72

A new successive system for the hydrogenation of styrene using a Pd sheet electrode is reported. The activated H atoms are electrochemically produced at the front side of the Pd sheet electrode and supplied through it to be used for hydrogenation at the back surface of the Pd sheet electrode. Only ethylbenzene was produced, and the production rate depended on the applied current. The current efficiency of > 93% occurred at an applied current of 10 mA.

Voltammetric Study of the Immobilization of Palladium at the Surface of Carbon Paste Electrodes

K.-H. LUBERT, M. GUTTMANN and L. BEYER, *Electroanalysis*, 1996, 8, (4), 320–325

Cyclic voltammetric studies were performed of Pd immobilisation at the surface of unmodified C paste electrodes. During pretreatment at 0 V, Pd was bound at the surface of the C paste, and the amount of immobilised Pd depended on the composition of the solution, polarisation time, electrode potential and stirring. During an anodic scan, the surface-bound Pd was oxidised at ~ + 0.6 V and the well-shaped peaks could be utilised for the determination of the immobilised Pd. The detection limit was ~ 5 × 10⁻⁶ M Pd²⁺ after 5 min polarisation at 0 V with stirring. Pd and H can be “deposited” simultaneously at the C paste surface through cathodic polarisation.

Rapid Oxidation of Ru(NH₃)₆³⁺ by Os(bpy)₃³⁺ within Nafion Coatings on Electrodes

M. SHI and F. C. ANSON, *Langmuir*, 1996, 12, (8), 2068–2075

When Ru(NH₃)₆³⁺ (1) and Os(bpy)₃³⁺ (2) reactants are incorporated in Nafion coatings on electrodes, the oxidation of (1) by (2), which is normally a very slow process, can proceed much more rapidly, especially with Nafion coatings that are not fully hydrated. The Ru(NH₃)₆³⁺ is oxidised to Ru(VII) at a rate that is first order in Ru(NH₃)₆³⁺ and Os(bpy)₃³⁺, and inverse first order in H⁺. The higher reaction rate obtained upon incorporation of the reactants into Nafion results from their higher concentrations rather than from enhancement in the intrinsic redox reactivity of either cation.

Electrochemical Behavior of the RuO₂/TiO₂ Anodes during the Electrolysis of Sea Water

C. LIANG and Q. GU, *Corros. Sci. Prot. Technol. (China)*, 1996, 8, (2), 125–129

Studies of the electrochemical behaviour of the anode RuO₂/TiO₂ during the electrolysis of sea water showed that use of the anode could improve current efficiencies and decrease energy consumption. The best results were obtained at current density of 100 mA/cm² and electrode gap of 5 mm. The cathode was electrochemically protected at potentials from - 820 to ~ -1450 mV (SCE).

Investigation of the Formation of RuO₂-Based Mixed Oxide Coatings by Secondary Ion Mass Spectrometry

S. DAOLIO, J. KRISTÓF, C. PICCIRILLO, C. PAGURA and A. DE BATTISTI, *J. Mater. Chem.*, 1996, 6, (4), 567–571

The evolution of a RuO₂-TiO₂ film electrode with temperature was studied using a coating mixture prepared on a Ti support from an isopropyl alcohol solution of hydrated Ru chloride and Ti diisopropoxide bispentane-2,4-dionate precursors. Concentration depth profiles monitored film evolution and identified surface segregation phenomena resulting from the increased metal dispersity.

PHOTOCONVERSION

The Role of Acidity in the Photoreaction of Carboplatin

W. LIU, Y. YANG, H. XIONG and Z. QUE, *Precious Met. (China)*, 1996, 17, (1), 19–22

Photochemical studies of acidic solutions of carboplatin on irradiation at 313nm showed that the photolytical product is *cis*-[Pt(NH₃)₂(H₂O)₂]²⁺ and the quantum yield is 0.89. Acidity is a major factor in the photoreaction of carboplatin and the mechanism is discussed.

Vibrational Sidelines in the Localized ³MLCT Emission of [Ru(bpy)₂(bpz)]²⁺ in [Zn(bpy)₂](ClO₄)₂ (bpy = 2,2'-Bipyridine, bpz = 2,2'-Bipyrazine)

H. RIESEN, L. WALLACE and E. KRAUSZ, *J. Phys. Chem.*, 1996, 100, (11), 4390–4394

The luminescence spectrum of [Ru(bpy)₂(bpz)]²⁺ (1) and [Ru(bpy-d₄)₂(bpz)]²⁺ complexes in the host [Zn(bpy)₂](ClO₄)₂ (2) was studied and sidelines associated with the spectator bpy/bpy-d₄ ligands were identified over the entire vibrational frequency range. Although the lowest excited ³MLCT states in Ru diimine systems are localised, the coupling in the ³MLCT excitations is 3–4 orders of magnitude larger. Dominant sidelines reported earlier for (1) in (2) are caused by contamination by [Os(bpy)₂(bpy-d₄)]²⁺.

Photosensitization of Nanocrystalline Semiconductor Films. Modulation of Electron Transfer between Excited Ruthenium Complex and SnO₂ Nanocrystallites with an Externally Applied Bias

P. V. KAMAT, I. BEDJA, S. HOTCHANDANI and L. K. PATTERSON, *J. Phys. Chem.*, 1996, 100, (12), 4900–4908

The charge injection from excited Ru(bpy)₂(dcbpy)²⁺, Ru(II), into SnO₂ nanocrystallites was studied by *in situ* spectroelectrochemical measurements. Laser flash photolysis of Ru(II)-modified SnO₂ nanocrystalline film was used to record the transient absorption spectra at different applied potentials. The yield of electron transfer product, Ru(III), decreased as the applied bias was switched to negative potentials. At a bias of -0.7 V, Ru(II)* was the only observed transient.

ELECTRODEPOSITION AND SURFACE COATINGS

Characterization of a Colloidal Pd(II)-Based Catalyst Dispersion for Electroless Metal Deposition

W. J. DRESSICK, L. M. KONDRACKI, M.-S. CHEN, S. L. BRANDOW, E. MATIJEVIĆ and J. M. CALVERT, *Colloid. Surf. A: Physicochem. Eng. Aspects*, 1996, 108, (1), 101–111

An aqueous Pd(II) dispersion for the selective electroless deposition of Ni at ligand-bearing surfaces, was prepared by hydrolysis of PdCl₂ at pH 5 in NaCl solution. The dispersion comprised anionic and uncharged Pd(II) species, from monomeric to colloidal, with colloidal species starting the electroless metal deposition. The colloidal catalysts have a diameter ~ 4–53 nm, with an average size of 30 ± 12 nm.

Electroplated Palladium Coating as a Nickel Migration (Thermal) Barrier

J. K. LIM, J. S. RUSSO and E. ANTONIER, *Plat. Surf. Finish.*, 1996, 83, (3), 64–67

Ni-Co plated chip carriers were coated with an acid Pd strike and electrolytic Pd deposits, using three different plating combinations: Ni-Co/Au (Pd strike), Ni-Co/Pd and Ni-Co/Pd/Au. Ni-Co/Au plated carriers were the standard. The tested samples showed equivalent or better Ni migration and solderability than the standard, that is, less than 10 at.% Ni migration and nearly 100% solder flow.

APPARATUS AND TECHNIQUE

Flow Injection Amperometric Detection of Ammonia Using a Polypyrrole-Modified Electrode and Its Application in Urea and Creatinine Biosensors

M. TROJANOWICZ, A. LEWENSTAM, T. KRAWCZYŃSKI, V. KRAWCZYK, I. LÄHDESÄKI and W. SZCZEPEK, *Electroanalysis*, 1996, 8, (3), 233–243

Amperometric NH₃ detection, using an anodically polarised Pt electrode, modified with PPy, was used in biosensors. NH₃ detection in a flow injection system with ≤ 100 μM of analyte at a detection limit of 0.6 μM was used to detect urea and creatinine by immobilising urease and creatinine iminohydrolase, respectively, at the PPy surface. A biosensor of very low sensitivity was obtained by urease entrapment in the PPy layer during electropolymerisation.

Effect of Electrode Materials on the Sensitive Properties of the Thick-Film Ceramic Humidity Sensor

W. QU, *Solid State Ionics*, 1996, 83, (3, 4), 257–262

A thick-film humidity sensor with excellent stability was produced by depositing a humidity sensitive layer between two metal electrodes on an Al₂O₃ substrate. The sensor response depended on the sensing layer and the properties of the electrode material. Pt electrodes gave higher sensitivity over the whole humidity range, and faster response than Ag/Pd electrodes.

Composite Pd/Ta Metal Membranes for Hydrogen Separation

N. M. PEACHEY, R. C. SNOW and R. C. DYE, *J. Membrane Sci.*, 1996, 111, (1), 123–133

A composite metal membrane was fabricated by vapour deposition using 13 μm Ta foils cleaned by ion milling, then coated with 1 μm of Pd metal on each side. The membrane of area $\sim 2\text{ cm}^2$, gave exceptionally high H₂ gas fluxes from 18.7 standard cm^3/min (sccm) at 300°C to 27.4 sccm at 365°C with a H₂ differential pressure of ~ 355 torr. The deposited Pd films were oriented along the (111) crystal axis.

HETEROGENOUS CATALYSIS

Deep Hydrodesulfurization of DBT and Diesel Fuel on Supported Pt and Ir Catalysts

R. NAVARRO, B. PAWELEC, J. L. G. FIERRO, P. T. VASUDEVAN, J. F. CAMBRA and P. L. ARIAS, *Appl. Catal. A: Gen.*, 1996, 137, (2), 269–286

Deep hydrodesulfurisation (HDS) of dibenzothiophene (DBT) and diesel fuel (with 0.08 wt.% S) was performed using Pt- and Ir/amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ (ASA) and on a stabilised HY zeolite. The normalised activities of Pt/ASA and Pt/HY catalysts were better than those of the Ir catalysts, with the HDS being dominant over hydrogenation. In HDS of diesel fuel (at 623 K), both Pt catalysts were a little more active than a commercial Co-Mo/Al₂O₃ catalyst. The normalised activity for HDS of DBT (593 K) increased as: Pt/HY > Pt/ASA >> Ir/HY > Ir/ASA, and the HDS of diesel fuel (623 K) increased as: Pt/HY >> Pt/ASA >> Ir/HY > Ir/ASA.

Regioselective Hydrogenation of Alkenes over Pt-Loaded Zeolite BEA

E. J. CREYGHTON, R. A. W. GROTENBREG, R. S. DOWNING and H. VAN BEKKUM, *J. Chem. Soc., Faraday Trans.*, 1996, 92, (5), 871–877

The hydrogenation of dec-1-ene (1) and (*E*)-dec-5-ene (2) was studied over Pt/Na-BEA and non-zeolitic Pt catalysts. Under specific conditions using Pt/Na-BEA, (1) is hydrogenated 18 times faster than (2), whereas the ratio is only ~ 2 for Pt on non-microporous supports. Compared with Pt/Na-BEA, Pt/amorphous meso/macroporous support shows a higher activity in the catalytic hydrogenation of (1) and (2) but a much lower regioselectivity. The hydrogenation over Pt/Na-BEA deviates from zero-order kinetics.

Kinetic Modeling of CO Oxidation on Pt/CeO₂ in a Gradientless Reactor

M. A. SHALABI, B. H. HARJI and C. N. KENNEY, *J. Chem. Tech. Biotechnol.*, 1996, 65, (4), 317–324

Pt/CeO₂ was studied in order to understand the promoting effects of CeO₂ in the CO oxidation reaction, at 100–170°C. At low concentrations of reactants, Pt/CeO₂ exhibited multiple steady states, similar to the multiplicity behaviour of Pt/Al₂O₃. CeO₂ lowers the activation energy for CO oxidation, increases the activity of the reaction by being a good O₂ store and suppresses the usual CO inhibition effect.

Synthesis and Characterization of Sol-Gel Pt/TiO₂ Catalyst

E. SÁNCHEZ, T. LÓPEZ, R. GÓMEZ, BOKHIMI, A. MORALES and O. NOVARO, *J. Solid State Chem.*, 1996, 122, (2), 309–314

Pt/TiO₂ catalysts with 1.0 wt.% Pt were prepared in a one-step operation by the sol-gel technique with Ti(OBu)₄ and Pt acetylacetonate, without any reduction of the sample in H₂. The fresh samples had three nanophases: rutile (the majority), anatase and Pt. Pt promoted the formation of rutile, either due to the presence of an intermediate PtO₂ phase, having the rutile structure, or to the Pt-catalysed dehydroxylation of anatase. Pt atoms do not enter into the crystalline structure of rutile, despite both PtO₂ and rutile having the same crystalline structure.

Crotonaldehyde Hydrogenation over Bimetallic Pt-Sn Catalysts Supported on Pregraphitized Carbon Black. Effect of the Sn/Pt Atomic Ratio

F. COLOMA, A. SEPÚLVEDA-ESCRIBANO, J. L. G. FIERRO and F. RODRÍGUEZ-REINOSO, *Appl. Catal. A: Gen.*, 1996, 136, (2), 231–248

Three bimetallic Pt-Sn/C catalysts, prepared by successive impregnation of pregraphitised C black with an aqueous solution of hexachloroplatinic acid and Sn(II) chloride, were studied during crotonaldehyde hydrogenation. When Sn was added to the samples, the amount of surface Pt was greatly reduced. Both Pt⁰ and Pt^I were detected by XPS in the fresh bimetallic catalysts. After reduction in flowing H₂ at 623 K, Pt was completely reduced to metal, and some Sn was reduced to Sn⁰, possibly allowing Pt-Sn alloy formation. Catalytic activity for gas phase hydrogenation of crotonaldehyde was greatly improved by Sn.

A Pt-Rh Synergism in Pt/Rh Three-Way Catalysts

Z. HU, *Chem. Commun.*, 1996, (7), 879–880

Performances of Pt, Rh and Pt/Rh catalysts were assessed after ageing in exhaust to mimic in-use catalyst operation. The activity of the Pt/Rh catalyst was about one order of magnitude higher than either a Pt or an Rh catalyst for HC/CO/NO three-way conversions. This high activity of the Pt/Rh three-way catalyst is attributed to a Pt-Rh synergism. The Pt/Rh/Al catalyst also gives HC/CO conversions of 50% at temperatures 70 K lower than the Pt/Al catalyst and lower than the Rh/Al catalyst by 100 K.

Structure and Catalysis of a SiO₂-Supported Gold-Platinum Cluster [(PPh₃)Pt(PPh₃Au)₆](NO₃)₂

Y. YUAN, K. ASAKURA, H. WAN, K. TSAI and Y. IWASAWA, *Chem. Lett. Jpn.*, 1996, (2), 129–130

A Pt catalyst [(PPh₃)Pt(AuPPh₃)₆](NO₃)₂ (1)/SiO₂ was very active for H₂-D₂ equilibration with a TOF of 29.8/s, but had low activity for ethene hydrogenation and CO oxidation at 303 K. Pt atoms bonded to Au atoms in the cluster. The cluster framework of (1)/SiO₂ was stable during the reactions at 303 K. The number of Au-Pt bonds fell after heat treatment.

The Shape-Selectivity of Activated Carbon Fibers as a Palladium Catalyst Support

H. JIN, S.-E. PARK, J. M. LEE and S. K. RYU, *Carbon*, 1996, 34, (3), 429–431

Activated C fibre (ACF) was used as a shape-selective catalyst support for Pd. Pd was deposited on pitch-based ACF and was used as the catalyst in the liquid-phase heterogeneous hydrogenation of olefinic C₆ hydrocarbons. As the adsorption capacity increased, the pore size distribution became wider, and mesopores and wider micropores increased. HNO₃ treatment and Pd loadings did not greatly affect the types of adsorption isotherm. For 1-hexene, the hydrogenation rate was a function of mean pore radius: the reaction does not occur at a mean pore radius of < 0.9, but for > 0.9 the reaction rate increased considerably. Shape-selectivity occurs inside the pores.

Liquid Phase Hydroformylation of Ring Substituted Styrenes Catalyzed by Rh-B and Rh-Zn-B Systems Supported on Silica

M. LENARDA, R. GANZERLA, S. PAGANELLI, L. STORARO and R. ZANONI, *J. Mol. Catal. A: Chem.*, 1996, 105, (3), 117–123

Rh based catalysts/SiO₂ were prepared by low temperature reduction of the preadsorbed salts with NaBH₄ and Zn(BH₄)₂. A remarkable B and Zn surface enrichment was observed from ESCA data in both catalysts. Both catalysts were active in the hydroformylation of liquid phase ring-substituted styrenes. The resulting reaction was really heterogeneous as no catalyst leaching occurred. The chemoselectivity was always close to 100%, and regioselectivity appeared to be controlled by the nature of the ring substituents.

Synthesis of Cyclopentanone Derivatives with Polystyrene-Supported Cyclopentadienyl Rhodium Catalysts

D. P. DYGUTSCH and P. EILBRACHT, *Tetrahedron*, 1996, 52, (15), 5461–5468

A polystyrene-supported η⁵-cyclopentadienyl Rh catalyst was applied to two different methods of cyclopentanone synthesis. The synthesis of substituted cyclopentanones was performed either by hydrocarbonylative cyclisation, starting from 1,4-dienes or from allyl vinyl ethers via tandem Claisen rearrangement, and intramolecular hydroacylation of the 4-pentenal intermediates. The polymer-attached CpRh(cod) complex was a very efficient and reusable hydroformylation catalyst.

Ruthenium Catalyst Supported on CeO₂ for Ammonia Synthesis

Y. NIWA and K.-I. AIKA, *Chem. Lett. Jpn.*, 1996, (1), 3–4

Lanthanide oxides, Sm₂O₃, La₂O₃, especially CeO₂, were more effective, when supporting Ru catalysts, rather than being a dopant during NH₃ synthesis. The activity of Ru/La₂O₃ catalyst was superior to other metal oxide-supported Ru catalysts, such as Ru/MgO. The activity, Ru dispersion, BET surface area and the amount of H consumption by Ru/CeO₂ depended on H₂ treatment, thus suggesting a SMSI phenomenon. Partially reduced CeO₂ donated electrons to Ru atoms, which then formed the active sites.

A Novel Basic Alkaline-Earth Zeolite-Supported Ruthenium Catalyst for Ammonia Synthesis

C. T. FISHEL, R. J. DAVIS and J. M. GARCES, *Chem. Commun.*, 1996, (5), 649–650

Studies of the promotional effect of alkaline-earth cations on the catalytic activity of Ru/zeolites during NH₃ synthesis showed an increase in the reaction rates that exceeds those for analogue catalysts containing only alkali-metal cations. The Ru clusters were supported on basic zeolite using as a starting material KX, CsX, CaX, BaX and MgO. Ru/BaX and Ru/CaX catalysts were three times more active than Ru/CsX; this is the highest value for zeolites in NH₃ synthesis.

Carbon Monoxide Hydrogenation on Supported Manganese-Ruthenium Catalysts

T. TERCIOGLU and J. F. AKYURTLU, *Appl. Catal. A: Gen.*, 1996, 136, (2), 105–111

CO hydrogenation over 6.3% Mn-2.5% Ru/Al₂O₃ catalyst was studied in a flow system with a differential fixed-bed reactor operating under atmospheric pressure at 553–613 K, H₂:CO = 1:3 and space velocity 5100–27,600 cm³/gh. Modification with Mn resulted in a shift of the product distribution to lower olefins. The activity and selectivity of the catalyst changed at/below and above 573 K. It is suggested that at/below 573 K, monolayer C deposits and > 573 K multilayer C deposits affect the performance of the catalyst.

Hydrogenation of Citral and Cinnamaldehyde over Bimetallic Ru-Me/Al₂O₃ Catalysts

G. NERI, L. MERCADANTE, C. MILONE, R. PIETROPAOLO and S. GALVAGNO, *J. Mol. Catal. A: Chem.*, 1996, 108, (1), 41–50

Hydrogenations of citral and cinnamaldehyde were studied over Ru-Me/Al₂O₃ catalysts, where Me = Ge, Sn or Pb. Two series of catalysts were prepared by using the controlled surface reaction (CSR) technique (RuEC series) and the more conventional co-impregnation method (RuNI series). Addition of Ge increased the catalytic activity of the RuEC series, but had no effect on RuNI series. Addition of Sn universally increased both activity and selectivity. The Pb present did not modify the selectivity and slightly decreased the catalytic activity on RuNI series samples.

HOMOGENEOUS CATALYSIS

Intramolecular Heck-Type Reactions in Aqueous Medium. Dramatic Change in Regioselectivity

S. LEMAIRE-AUDOIRE, M. SAVIGNAC, C. DUPUIS and J.-P. GENÉT, *Tetrahedron Lett.*, 1996, 37, (12), 2003–2006

Intramolecular Heck-type cyclisations promoted by Pd(OAc)₂/TPPTS and PdCl₂/TPPTS catalytic systems, in CH₃CN/H₂O medium, are reported. The cyclisations were efficiently performed in aqueous medium. Unexpected endo selectivity was observed rather than the usual exo process, the reaction reversing in favour of the endo cyclised compounds. Either endo or exocyclic closure can be obtained from the same substrate.

Mild Azide-Mediated Palladium-Catalysed Cleavage of Allyloxy-carbonyl Protected Alcohols in Aqueous Media

S. SIGISMONDI and D. SINOU, *J. Chem. Res. (S)*, 1996, (1), 46–47

The deprotection of allyloxy-carbonyl-protected alcohols was efficiently performed under neutral conditions using Pd(OAc)₂-tppts catalyst in MeCN-H₂O, in the presence of NaN₃ as allyl scavenger. The deprotection reaction proceeded smoothly with *alloc*-primary and *alloc*-secondary alcohols, giving quite good yields. The H₂O-soluble catalyst can be easily reused without the addition of more nucleophile.

An Improved Procedure for the Synthesis of Substituted Acetylenes from the Reaction of Acetylene Gas with Aryl Iodides under Palladium-Copper Catalysis

M. PAL and N. G. KUNDU, *J. Chem. Soc., Perkin Trans. I*, 1996, (5), 449–451

The use of dimethylformamide (DMF) as a solvent promoted the Pd-Cu catalysed reaction of acetylene gas with aryl iodides in a closed system to give disubstituted acetylenes in fair to excellent yields. The reaction was carried out in the presence of [Pd(PPh₃)₂]Cl₂, Et₃N and CuI in DMF in acetylene gas. When chloroform was used as the solvent, mixtures of mono- and disubstituted acetylenes were produced; some of these have biological interest.

Synthesis and Characterization of Poly(ethynyltrimethylsilane) Containing Pd(II) Coordination Sites

M. V. RUSSO, A. FURLANI, M. CUCCU and G. POLZONETTI, *Polymer*, 1996, 37, (9), 1715–1722

Polymerisation reaction of ethynyltrimethylsilane (HC≡C-Si(CH₃)₃) are reported in the presence of the bis(acetylide) complex {Pd[C≡C-Si(CH₃)₃]₂(PPh₃)₂} in 1:100; 1:50 and 1:25 catalyst : monomer ratios. The catalyst plays different roles, such as activation by Pd of the triple C≡C bond of the monomer and insertion into the Pd-C σ-bond with growth of the polymer chain; oxidation of PPh₃ to OPPh₃, which can be released leaving free co-ordination sites on Pd followed by crosslinking with the C=C bonds of neighbouring polymer chains; and in the presence of NH(C₂H₅)₂, the C-Si bond is activated followed by substitution of some Si(CH₃)₃ groups with N(C₂H₅)₂.

Hydroformylation of Unsaturated Alcohols Catalyzed by Rh(acac)(CO)₂ Modified with Different Phosphorus Ligands

A. M. TRZECIAK, E. WOLSZCZAK and J. J. ZIÓLKOWSKI, *New J. Chem.*, 1996, 20, (3), 365–370

The activity of Rh(acac)(CO)₂ catalysts modified with mono- and diphosphorus ligands of different electronic and steric properties was studied during hydroformylation of unsaturated alcohols at 60–80°C under 10 atm H₂/CO = 1. The reaction of the 3-buten-2-ol and 1-octen-3-ol yielded the cyclic 2-hydroxy-5-methyltetrahydrofuran and 2-hydroxy-5-pentyltetrahydrofuran, respectively. Ph₂P(CH₂)₄PPh₂ and P(O-*m*-MeC₆H₄)₂ gave the highest catalytic activity.

Direct Formation of Alcohols by Hydrocarbonylation of Alkenes under Mild Conditions Using Rhodium Trialkylphosphine Catalysts

J. K. MACDOUGALL, M. C. SIMPSON, M. J. GREEN and D. J. COLE-HAMILTON, *J. Chem. Soc., Dalton Trans.*, 1996, (6), 1161–1172

The hydroformylation of hex-1-ene to heptanal and 2-methylhexanal in toluene was catalysed by the complex [RhH(PEt₃)₃], while in tetrahydrofuran significant amounts of heptanal and 2-methylhexanal were formed, especially over long reaction times. In protic solvents only alcohols were produced even after short reaction times. The reactions were very rapid and occurred readily with alkenes. The highest rates were observed for ethene (54,000 turnovers/h) and the products were always alcohols. A new mechanism for this direct hydrocarbonylation is proposed.

Catalytic Alkane Dehydrogenation by IrClH₂(PPr^t)₂: Evidence for an Alkane Associative Mechanism

J. BELLI and C. M. JENSEN, *Organometallics*, 1996, 15, (6), 1532–1534

The dehydrogenation of alkanes to alkenes was catalysed by IrClH₂(PPr^t)₂ in the presence of the H acceptor, *tert*-butylethylene, at 150°C. Mechanistic studies, including labelling experiments with IrClD₂(PPr^t)₂, showed that reversible co-ordination and hydride migration to *tert*-butylethylene is facile and that the slower, subsequent elimination of *tert*-butylethane required prior co-ordination of alkane.

Ru-Catalyzed Hydrogenolysis of Chiral Allylic and Propargylic Cyclic Carbonates: Synthesis of Optically Active (*E*)-Allylic and Allenic Alcohols

S.-K. KANG, D.-Y. KIM, H.-S. RHO, S.-H. YOON and P.-S. HO, *Synth. Commun.*, 1996, 26, (8), 1485–1492

Optically active (*E*)-allylic, (*E,E*)-dienylic and allenic alcohols were synthesised with excellent regioselectivity by RuH₂(PPh₃)₄ (1) catalysed reductive cleavage of chiral allylic cyclic carbonates with NH₄ formate. Also, hydrogenolysis of propargylic cyclic carbonates by (1) afforded only allenic alcohols.

FUEL CELLS

The Chemical State of Sulfur in Carbon-Supported Fuel-Cell Electrodes

K. E. SWIDER and D. R. ROLISON, *J. Electrochem. Soc.*, 1996, 143, (3), 813–819

The chemical state of S in Pt/C electrocatalysts, using vulcan C, was studied by measuring its oxidation state by XPS during the preparation of a “mock” fuel-cell electrode to find if the S from the C affects the electrocatalyst. Pt catalytically oxidised some of the covalent S in the vulcan C to sulphate when H₂O, heat and strong physical contact between Pt and C were all present. However, most of the zero-valent S remained in the C after treatment, without any initial contact with Pt, so may be a source of Pt poisoning.

Analysis of Reaction Kinetics for Carbon Monoxide and Carbon Dioxide on Polycrystalline Platinum Relative to Fuel Cell Operation

R. J. BELLOWS, E. P. MARUCCHI-SOOS and D. T. BUCKLEY, *Ind. Eng. Chem. Res.*, 1996, 35, (4), 1235-1242

Hydrogen can be produced in a polymer electrolyte fuel cell by reforming hydrocarbons or alcohols. Such H₂ contains CO and CO₂ (CO_x) impurities which adsorb onto the Pt anode electrocatalyst, reducing the efficiency for H₂ electro-oxidation. Studies showed that the rate of CO electro-oxidation is an important factor in determining the CO tolerance of Pt anodes. It is suggested that for CO tolerance, all CO in the feed must be effectively consumed during electro-oxidation at low potentials; CO adsorption fluxes will be much faster than CO₂ electroreduction on Pt.

Work Function Variations and Oxygen Conduction in a Pt|ZrO₂(Y₂O₃)|Pt Solid Electrolyte Cell

N. G. TORKELSEN and S. RAAEN, *Appl. Surf. Sci.*, 1996, 93, (3), 199-203

The working electrode in a Pt|ZrO₂(Y₂O₃)|Pt solid electrolyte cell was studied by photoelectron spectroscopy in UHV, and changes in the electrode work function were correlated with the O ion transport through the cell. The change in work function was independent of the cell temperature, when the cell operated as an O conductor. Negative O species at the working electrode during O pumping were indicated.

CHEMICAL TECHNOLOGY

Preparation of Pd/Ceramic Composite Membrane. I. Improvement of the Conventional Preparation Technique

A. LI, G. XIONG, J. GU and L. ZHENG, *J. Membrane Sci.*, 1996, 110, (2), 257-260

An improved method of making Pd/ceramic composite membranes has been developed. Thin Pd films were deposited on the surface of a porous ceramic substrate by the conventional and the improved electrodeless plating technique. The improved method pre-seeds Pd nuclei in a new way: Pd²⁺ modified by γ -AlOOH sol is deposited on the surface of the porous Al₂O₃ disk support by a slip-casting process, calcined in air, then the Pd ion in the top layer is reduced to metallic Pd in H₂ for 2 h at 400°C. The Al₂O₃ membrane + Pd nuclei is then electrodelessly plated in a Pd bath.

Sonochemical Preparation of Ultrafine Palladium Particles

K. OKITSU, H. BANDOW and Y. MAEDA, *Chem. Mater.*, 1996, 8, (2), 315-317

Ultrafine Pd particles were prepared by using ultrasound to reduce tetrachloropalladate ions in aqueous solutions. Stable fine particles of Pd were readily produced in the presence of a protective agent, such as a surfactant or a H₂O-soluble polymer. The Pd particles obtained were very fine and their sizes had only a narrow distribution in the range of several nanometres.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pt/PZT/n-SrTiO₃ Ferroelectric Memory Diode

K. GOTOH, H. TAMURA, H. TAKAUCHI and A. YOSHIDA, *Jpn. J. Appl. Phys.*, 1996, 35, (1A), 39-43

A non-volatile ferroelectric memory was fabricated from vertical metal-ferroelectric-semiconductor diodes with simpler structure than a ferroelectric random access memory (FRAM) cell. It operates at a lower voltage than metal ferroelectric semiconductor field effect transistors or flash memories. The correct non-volatile and non-destructive memory read-outs were shown with the Pt/PZT/n-SrTiO₃ diode. The write voltages were -5 V to write a logic "0" and > 2.5 V to write a logic "1". The read voltage was 0.8 V.

Material and Electrical Characteristics of Iron Doped Pt-InAlAs Schottky Diodes Grown by LP-MOCVD

K. HONG, D. PAVLIDIS and F. SÉJALON, *J. Electron. Mater.*, 1996, 25, (4), 627-632

The effect of Fe doping on electrical properties and on noise characteristics of devices was studied using Pt-Schottky diodes fabricated on undoped and Fe-doped InAlAs. Fe-doped InAlAs showed a Lorentzian component in the noise spectra not found in undoped materials. An activation energy of ~0.77 eV was found for traps due to Fe incorporation, using temperature dependent low frequency noise measurements.

Barrier Characteristics of PtSi/p-Si Schottky Diodes as Determined from I-V-T Measurements

P. G. MCCAFFERTY, A. SELLAI, P. DAWSON and H. ELABD, *Solid-State Electron.*, 1996, 39, (4), 583-592

The current-voltage-temperature characteristics of PtSi/p-Si Schottky barrier diodes were measured at 60-115 K. Deviation of the ideality factor from unity below 80 K was modelled using the so-called T₀ parameter with T₀ = 18 K as an inhomogeneous Schottky contact. A mean barrier height at T = 0 K, Φ_b^0 = 223 mV, with an assumed Gaussian distribution of standard deviation, σ_b = 12.5 mV was determined.

TEMPERATURE MEASUREMENT

Progress on Fabrication of Iridium-Gold Proximity-Effect Thermometers

J. HÖHNE, G. FORSTER, C. ABSMAIER, P. COLLING, S. COOPER, F. V. FEILITZSCH, P. FERGER, J. IGALSON, E. KELLNER, M. KOCH, M. LOIDL, U. NAGEL, F. PRÖBST, A. RULOFS and W. SEIDEL, *Nucl. Instr. Methods, Phys. Res. A*, 1996, 370, (1), 160-161

Ir-Au proximity-effect bilayers with critical temperatures 20-100 mK were made as superconducting phase transition thermometers for low temperature calorimeters. Film thickness for the Ir and Au films is controlled during evaporation to $\pm 3\%$ and varies < 15 Å at different positions on the film. The measured residual resistivity ratio of the Ir films is ~2 for substrate temperatures of 300°C and ~8 for 630°C.